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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius		L	liter
deg	degree		min	minute
g	gram		mL	milliliter
g/g	gram per gram		mt	metric ton
g/L	gram per liter		pct	percent
h	hour		wt pct	weight percent
in	inch		yr	year

ACID SULFATION OF ALUNITE

By L. J Froisland,[1] M. L. Wouden,[1]
and D. D. Harbuck[1]

ABSTRACT

The U.S. Bureau of Mines conducted laboratory studies on sulfuric acid (H_2SO_4) digestion of alunite [$KAl_3(SO_4)_2(OH)_6$] as a means for treating domestic deposits of this mineral. Digesting alunite ore in boiling H_2SO_4 at concentrations of 88-wt-pct acid or higher breaks down the alunite and permits a convenient separation of potassium and aluminum. The digestion reaction is a complex sulfation reaction occurring in two stages. In this reaction, the potassium component extracts into the H_2SO_4 for eventual recovery as potassium sulfate (K_2SO_4) in a separate unit operation. Aluminum is left as acid-insoluble aluminum sulfate [$Al_2(SO_4)_3$], which can be extracted by a 95° C water leach. Additional purification of $Al_2(SO_4)_3$ produced in this study is needed to meet cell-grade alumina (Al_2O_3) purity specifications. Extraction and separation of potassium and aluminum from the alunite ore were consistently above 90 pct.

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INTRODUCTION

Although aluminum is the most abundant metal in the Earth's crust, its only commercial ore is bauxite, a mixture of impure, hydrated aluminum oxides. Aluminum is one of four "controlled materials" in the U.S. Department of Commerce Defense Priorities and Allocation System (DPAS) (1);[2] the other three are steel, copper, and nickel. This designation requires suppliers to give priority to purchases of the controlled materials by Government agencies involved with national defense. Because of the critical and strategic nature of aluminum, stockpiles of bauxite have been established for purposes of national security.

One important part of the Bureau of Mines mission is to develop technology for using domestic resources and to reduce the Nation's dependence on foreign sources of critical and strategic materials. The total U.S. reserve base of bauxite, including marginally economic and some subeconomic resources, is about 40 million mt of ore, which is less than 1 pct of the world total (2). In 1986, domestic bauxite production was estimated to be 500,000 mt of ore, mined from surface mines in Alabama and Arkansas. Virtually all of this bauxite was processed into nonmetallic products such as abrasives and refractories. In 1986, U.S. net bauxite imports were estimated to be 97 pct of apparent consumption (3). Clearly, domestic bauxite resources are inadequate to meet U.S. aluminum demands, but this country does have virtually inexhaustible aluminum resources in materials other than bauxite. Successful development of technology to use these domestic nonbauxite resources could reduce our dependence on imported bauxite and would ensure a stable, long-term source of aluminum.

One of these alternative sources of aluminum is alunite, which occurs in several known deposits. Two large deposits are located in the Western United States. A deposit in southwestern Utah contains an estimated 118 million mt of proven alunite ore having an Al_2O_3 content of 10 pct or higher (4). A second, less well-delineated deposit is in central Colorado. Together, these two deposits contain an estimated 20 million mt or more of aluminum at grades of 9 to 15 pct. These two deposits could provide a 3- to 4-yr supply of aluminum at current domestic consumption rates.

H_2SO_4 processes for treatment of alunite were developed over 60 yr ago (5-6). In these early processes, alunite was digested in 20- to 75-wt-pct H_2SO_4 for up to 48 h at temperatures below 200° C. Sulfated components were leached into the acid and later recrystallized by evaporation and/or cooling. The crystals were then roasted to convert $Al_2(SO_4)_3$ and/or potassium alum $KAl(SO_4)_2$ to Al_2O_3, and the calcine was leached in water to remove K_2SO_4.

In 1934, Kalunite, Inc., patented a process known as the Kalunite process (7-8). The primary difference between this process and the earlier work was addition of K_2SO_4 in amounts sufficient to convert all of the aluminum content to $KAl(SO_4)_2$. This alum was then crystallized from solution, calcined, and leached as before.

In recent years, Soviet researchers have further modified the Kalunite process to reduce H_2SO_4 consumption and iron contamination of the Al_2O_3 product (9). Reduction of ferric ion to ferrous ion (Fe^{+3} to Fe^{+2}) before crystallization decreases iron contamination in the $KAl(SO_4)_2$ and conserves some of the H_2SO_4 formerly consumed in producing iron sulfates.

H_2SO_4 routes for obtaining Al_2O_3 from nonbauxite sources have all encountered severe process and economic problems preventing their adoption. Some of these problems are high energy costs in dehydration of the $Al_2(SO_4)_3$, very poor filtering characteristics of $Al_2(SO_4)_3$ slurries, and difficulty in meeting purification specifications. Because of these problems, H_2SO_4 routes have never been economically competitive with the Bayer process for bauxite (10-12). The current Bureau research does not resolve these problems, but it does present a method of breaking down the alunite structure and separating potassium from aluminum without going through the alum precipitation procedure. This report describes and summarizes the chemistry of treating alunite with hot, concentrated (>80 wt pct) H_2SO_4 and of water leaching the resultant sulfated material.

ALUNITE SAMPLE CHARACTERIZATION

Alunite ore samples were received from the two large deposits in the Western United States. Ore from the Utah deposit consisted of a fine-grained mixture of alunite and quartz in nearly equal proportions. Mineralogical examination indicated that liberation of quartz and alunite began at minus 100 mesh and was almost complete at minus 400 mesh. A sample of the Utah ore, which was received as

rocks ranging in size up to 6 in, was crushed to minus 10 mesh in preparation for experimentation. A screen analysis with chemical analyses of the screen fractions indicated uniform distribution of alunite throughout the size fractions. This crushed Utah ore was used for test work.

A sample of ore from the Colorado alunite deposit was obtained and characterized as an alunite-kaolinite mixture in a quartz matrix. The sample received was lower in aluminum grade than was the Utah sample; chemical analyses of ore samples from both deposits are shown in table 1.

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[2]Italic numbers in parentheses refer to items in the list of references at the end of this report.

TABLE 1. - Chemical analyses of Utah and Colorado alunite samples, weight percent

Component	Utah	Colorado	Component	Utah	Colorado
Al	9.2	5.5	Na	.3	NA
Ba	.03	0	P	.1	.1
Ca	1.1	.08	Pb	.04	0
Fe	1.4	1.2	SiO$_2$	41.1	65.1
K	3.7	2.2	SO$_4$	22.1	12.3
Mg	.1	.01	Tl	.1	.2

NA Not analyzed.

ALUNITE TREATMENT

Alunite reacts rapidly with hot, concentrated H$_2$SO$_4$ to form potassium and aluminum sulfates and water according to the overall reaction

$$2KAl_3(SO_4)_2(OH)_6 + 7H_2SO_4$$

$$\rightarrow 2KHSO_4 + 3Al_2(SO_4)_3 + 12H_2O. \qquad (A)$$
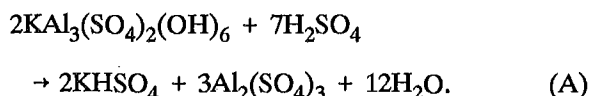
Water and the potassium components are soluble in the concentrated acid; the aluminum component and the gangue minerals are insoluble in the acid. Thus, a separation of potassium from aluminum occurs during the sulfation procedure. The aluminum component is then extracted in a water leach of the sulfation residue, and the insoluble gangue minerals are removed to waste. This sequence forms the initial treatment procedures for processing alunite.

Separate, detailed studies of the sulfation and water-leach procedures determined the effects of changes in operating conditions and made possible the selection of preferred conditions. This section of the report describes the procedures and results of bench-scale, batch-type studies of the sulfation and leach systems. Also presented are results from a short locked-cycle test program in which process solutions were recycled and Al$_2$(SO$_4$)$_3$ crystals were recovered from the aqueous leach solution.

ACID SULFATION

Batch-test procedures, effects of variable changes, and proposed sulfation mechanisms are described here for the H$_2$SO$_4$ digestion operations.

Sulfation Test Procedures

The sulfation test apparatus, depicted in figure 1, included a baffled 1-L reaction flask equipped with a stirrer, temperature probe, and a condenser with a trap to collect evaporated water. A tube was inserted into one of the top ports on the flask for periodic removal of slurry samples for analysis. The condenser was open to maintain atmospheric pressure within the reaction flask.

Sulfation tests were conducted by preheating various acid solutions in the reaction vessel to the desired temperature, adding alunite, and digesting the slurry for a specific time period. In all tests, 100 g of alunite ore was added to 500 mL of acid, which established the initial slurry mix at 200 g of ore per liter of acid. Samples of 50 to 100 mL of slurry were periodically removed to determine sulfation progress. These slurry samples were filtered; the solid residues were washed with 100 mL of fresh acid to remove entrained potassium; and the wash acid was added to the acid filtrate. The washed solids were water leached in a standard procedure at 95° C for 30 min with at least 5 mL of water per gram of sulfated solids to ensure complete dissolution of water-soluble components, and the water-leach solutions were filtered free of insoluble gangue minerals. (The volumes of acid used in the wash procedure and water used in the water-leach operation were for analytical purposes only and do not represent optimum
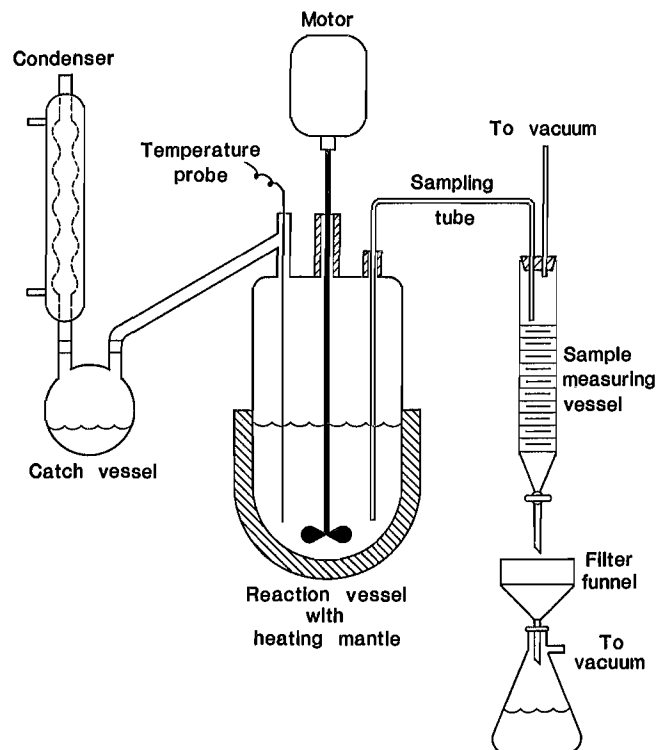

Figure 1.—Schematic of batch sulfation testing equipment.

volumes.) The acid filtrate plus wash acid, the water-leach solution, and the final filter residue were assayed to determine dissolution and separation of aluminum and potassium.

Initial acid solutions were prepared for each test by diluting concentrated (96-wt-pct) H_2SO_4 to the desired concentration with water. Nominal acid concentrations designated in this report refer to this diluted acid. If the initial acid solution for any particular test was to contain potassium, K_2SO_4 was added to the diluted acid in appropriate quantities.

Sulfation Results

Sulfation variables include time, particle size, acid concentration and temperature, and potassium concentration. Each variable was studied in a separate test program except for reaction time, which was an integral part of all test programs.

Effect of Particle Size

Utah ore initially at minus 10 mesh was crushed and sized into the following mesh fractions for sulfation testing: minus 100 plus 150, minus 150 plus 200, minus 200, minus 325, and minus 400. Material in each size fraction was sulfated in 91-wt-pct H_2SO_4 at 260° C. These conditions were selected because they had produced excellent results in preliminary tests. Extractions of potassium by the acid phase and aluminum by the water-leach solution are shown in figures 2 and 3 as functions of particle size and sulfation time.

The curves show rapid sulfation and extraction of elements during the first 15 min, followed by a gradual increase over the next 4 h. Although the smaller size particles yielded greater initial extraction rates, there were no significant differences in extractions between minus 200-, minus 325-, and minus 400-mesh material after 2 h of sulfation. Particle sizes larger than 200 mesh yielded decreased extractions of both potassium and aluminum; therefore, minus 200 mesh was determined to be the optimum particle size for alunite sulfation. Two hours of reaction time was sufficient in this test series to achieve 95-pct extraction of both potassium and aluminum.

Effect of Acid Concentration and Temperature

During sulfation, water, K_2SO_4, and other reaction products dissolve into the concentrated acid, effectively diluting it. Removing water by boiling helps to maintain the acid concentration; therefore, for each nominal acid concentration tested, a corresponding boiling temperature was maintained (13). Nominal acid concentrations ranged from 86- to 96-wt-pct H_2SO_4, with corresponding boiling temperatures of 227° to 300° C. Particle size of alunite feed in these tests was minus 200 mesh.
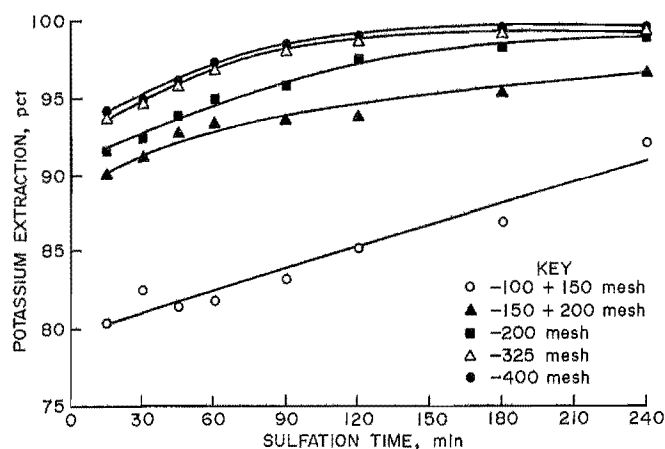
Figure 2.—Particle size effects on potassium extraction into process acid.
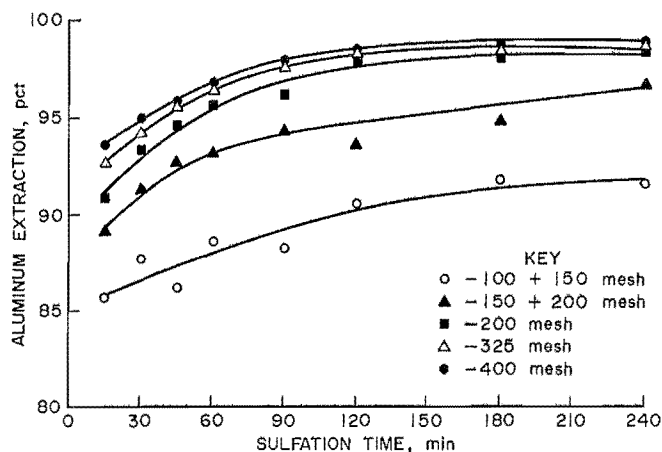
Figure 3.—Particle size effects on aluminum extraction into water-leach solution.

Potassium and aluminum extractions into the respective acid and water-leach solutions over the range of acid concentrations and boiling temperatures are shown in figures 4 and 5. These curves show that about 82 pct of the potassium was extracted by the acid and about 92 pct of the aluminum was extracted by the water-leach solution after 4 h of sulfation in 96-wt-pct acid at 300° C. Decreasing the acid concentration to 91 wt pct increased overall extraction of both components to between 92 and 93 pct in their respective solutions after only 30 min of sulfation and to about 98 pct after 2 h.

A further decrease in acid concentration to 88 wt pct had little effect on overall extraction of either element, but separation of aluminum and potassium decreased as the acid began to extract some of the aluminum, especially at the beginning of the sulfation. After 30 min of sulfation,
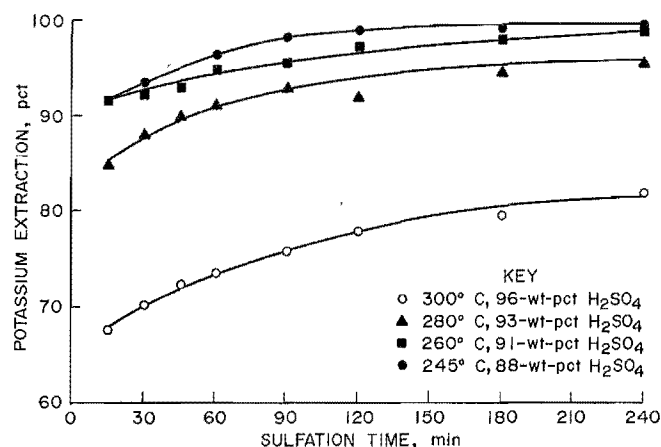
Figure 4.—Acid concentration and temperature effects on potassium extraction into process acid.
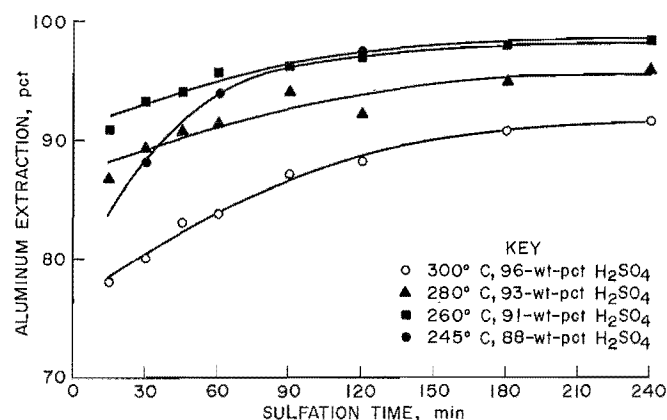
Figure 5.—Acid concentration and temperature effects on aluminum extraction into water-leach solution.

Figure 6.—Potassium distribution among products as a function of sulfation time in 86-wt-pct H_2SO_4 at 227° C.

total aluminum extraction from the ore was 95 pct, but only 88 pct was extracted into the water-leach solution. The remaining 7 pct was extracted into the process acid. After 2 h of sulfation, aluminum extraction was 96 pct into the water leach and 2 pct into the acid solution.

When the acid concentration was decreased still further, to 86-wt-pct H_2SO_4 boiling at 227° C, potassium appeared to form a water-soluble, acid-insoluble compound that slowly converted to the desired acid-soluble potassium compound. After 60 min of digestion, only 45 pct of the potassium reported to the acid and about 50 pct reported to the water-leach solution, as shown in figure 6. After 3 h, 95 pct of the potassium reported to the acid. Reasons for the dramatic shift in potassium distribution are discussed in the section "Interactions Between Potassium Concentration and Acid Concentration-Temperature Variables." Aluminum extractions from the sulfated residue during water leaching were similar to extractions achieved

after sulfation with 88-wt-pct H_2SO_4, except that 10 pct of the aluminum initially was extracted into the acid solution and remained there.

These batch-test results show that sulfation in 91-wt-pct H_2SO_4, maintained at a temperature of 260° C, yielded over 95-pct potassium and aluminum extraction and separation. More concentrated acid yielded lower overall extractions, and less concentrated acid yielded incomplete separations. However, as will be shown later, selection of a preferred acid concentration and temperature level is dependent on the potassium concentration in the acid. These variables were shown to have a complex interaction.

Effect of Potassium Accumulation in the Process Acid

Potassium accumulates in the concentrated H_2SO_4 solution as it is recycled in the sulfation process. This accumulation can affect the process in two ways: First, potassium accumulation affects the sulfation reaction; second, the accumulated potassium will eventually have to be removed from the acid. Sulfation effects are discussed here; removal is discussed in the section "Potassium Control."

Sulfation effects were determined by sulfating minus 200-mesh alunite ore in 91-wt-pct H_2SO_4 at 260° C with initial potassium concentrations in the acid varying from 0 to 100 g/L. Test results, presented in figure 7, clearly show that the time required for potassium extraction into the acid increased as the initial potassium concentration increased. With potassium concentrations below 20 g/L, potassium extraction was immediate. With 30 or 40 g/L concentration, extraction was delayed between 30 and 45 min. With 50 g/L concentration, the delay was between 60 and 90 min, while with 70 g/L concentration, the delay

6

Figure 7.—Initial potassium concentration effects on potassium extraction into process acid.

Figure 8.—Acid concentration and temperature effects on potassium extraction into process acid with initial potassium concentration of 70 g/L.

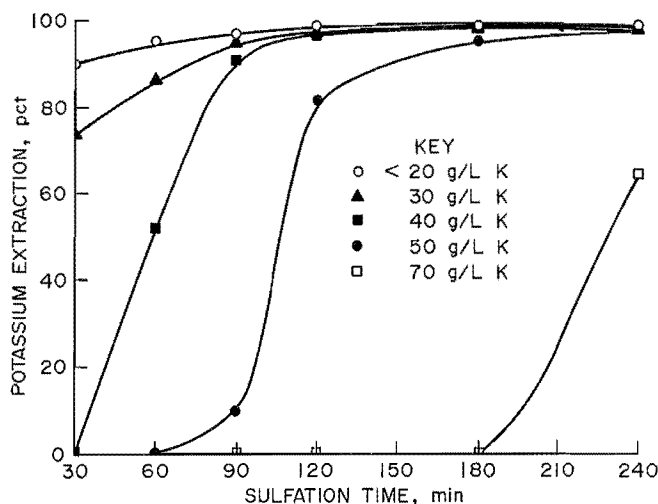was extended to over 3 h. Although not shown in figure 7, initial potassium concentrations greater than 80 g/L caused delays longer than 4 h.

Throughout this test series, total extraction of potassium and aluminum from the ore remained at 90 pct or higher after 2 h of digestion; only the separation of the two elements was affected by increasing potassium accumulation in the acid. Potassium not extracted into the acid reported with the aluminum in the water-leach solution.

Two preliminary conclusions were drawn from these potassium extraction results: (1) Potassium concentrations greater than 20 g/L in the acid delayed the extraction of additional potassium into the acid, and (2) the potassium concentration in the acid should be kept below 50 g/L to ensure complete separation of potassium and aluminum within 2 h. However, these conclusions were modified following investigation of the interaction between potassium concentration and acid concentration. This interaction is discussed in the next section.

Interactions Between Potassium Concentration and Acid Concentration-Temperature Variables

Preliminary conclusions, drawn from data presented in figures 4, 5, and 7, were (1) increasing the acid concentration and temperature combination above 91-wt-pct H_2SO_4 and 260° C decreased extractions of both potassium and aluminum, and (2) accumulation of potassium in the process acid to concentrations above 20 g/L caused delays in extraction of additional potassium into the acid. These two variables interact in a manner that modifies both of these conclusions.

The time required for potassium extraction into the acid with initial potassium concentrations above 20 g/L can be reduced by increasing the sulfation temperature and nominal acid concentration. Figure 8 shows the time
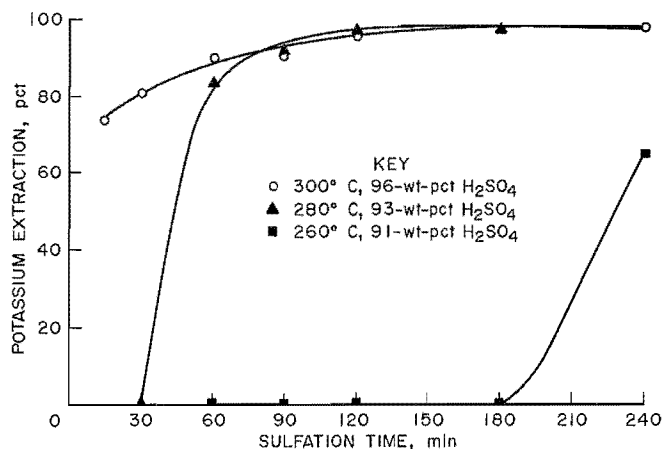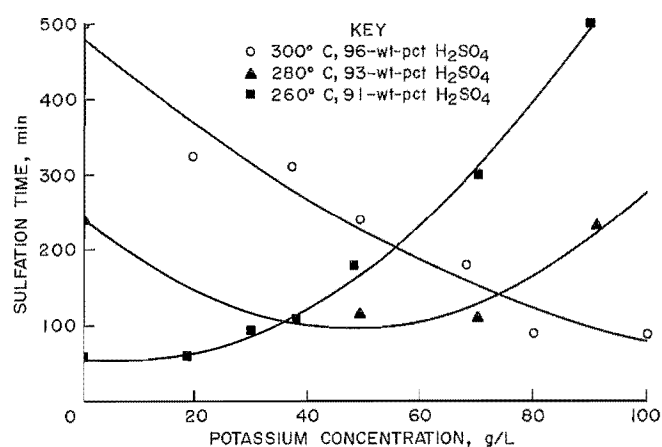
Figure 9.—Sulfation time required for 95-pct potassium extraction into process acid with increasing potassium concentrations and different acid concentration and temperature levels.

shift for extraction of potassium into acid with an initial concentration of 70 g/L potassium and nominal sulfation acid concentrations of 91, 93, and 96 wt pct with corresponding temperatures of 260°, 280°, and 300° C. As the sulfation temperature increases, less time is required to convert the potassium into an acid-soluble compound. At 260° C, the required time was over 3 h; at 280° C, it was reduced to 45 min; and at 300° C, it was less than 30 min.

Interactions between potassium concentration in the acid and the acid concentration-temperature combination are shown in figure 9. Time required to extract 95 pct of the potassium from the alunite into the process acid is plotted against initial potassium concentrations. Curves for three acid concentration and temperature combinations are shown. There is a complex relationship between time, acid concentration-temperature, and potassium levels that

determines the best potassium extraction in the shortest sulfation time. When the potassium concentration in the acid was below 35 g/L, the optimum acid concentration and temperature combination was 91-wt-pct acid and 260° C. With potassium concentrations between 35 and 75 g/L, a combination of 93-wt-pct acid and 280° C yielded faster potassium extraction; and when the potassium concentration was above 75 g/L, a combination of 96-wt-pct acid and 300° C appeared best. The next section discusses a reaction mechanism that may explain many of the variable effects determined in the batch tests.

Proposed Sulfation Reaction Mechanism

Reaction A may represent the overall chemistry of alunite sulfation, but X-ray diffraction (XRD) analysis of sulfated solids showed that $KAl(SO_4)_2$ is present as a solid during the period of time in which potassium extraction into the acid is delayed. The proposed sulfation mechanism, therefore, breaks reaction A into a two-stage sequential reaction with an intermediate $KAl(SO_4)_2$ product, as shown in reactions B and C.

$$KAl_3(SO_4)_2(OH)_6 + 3H_2SO_4 \rightarrow KAl(SO_4)_2$$

$$+ Al_2(SO_4)_3 + 6H_2O. \quad (B)$$

$$2KAl(SO_4)_2 + H_2SO_4 \rightarrow Al_2(SO_4)_3 + 2KHSO_4. \quad (C)$$
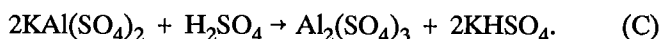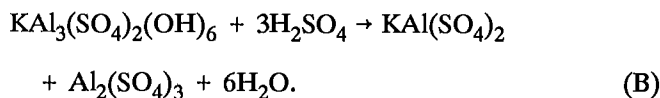
When potassium is present in the process acid, reaction B is altered, and the formation of $KAl(SO_4)_2$ is enhanced to yield reaction D.

$$KAl_3(SO_4)_2(OH)_6 + 2KHSO_4 + 2H_2SO_4$$

$$\rightarrow 3KAl(SO_4)_2 + 6H_2O. \quad (D)$$

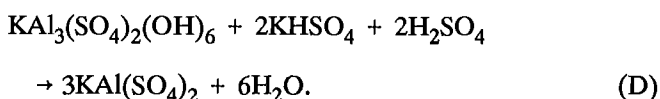XRD patterns (fig. 10) for solids sulfated at 260° C in nominal 90-wt-pct acid containing 50 g/L potassium in solution illustrate formation of $KAl(SO_4)_2$ and conversion to $Al_2(SO_4)_3$ during the sulfation process.

This two-stage reaction mechanism explains the complex interaction between acid concentration-temperature and potassium concentration. Sulfation data, coupled with XRD data, indicate that both reactions B and D occur rapidly, with virtually complete breakdown of the alunite structure within the first 30 min of sulfation. The rate of reaction C appears to be dependent on both acid concentration-temperature and potassium concentration in the acid, causing the potassium extraction delay observed in some tests. When reactions B and C occur together, a decrease in acid concentration and temperature from 96 wt pct and 300° C to 91 wt pct and 260° C shifts the equilibrium to the right and yields a more complete sulfation, as seen in figures 4 and 5. However, when the concentration and temperature variable is decreased below
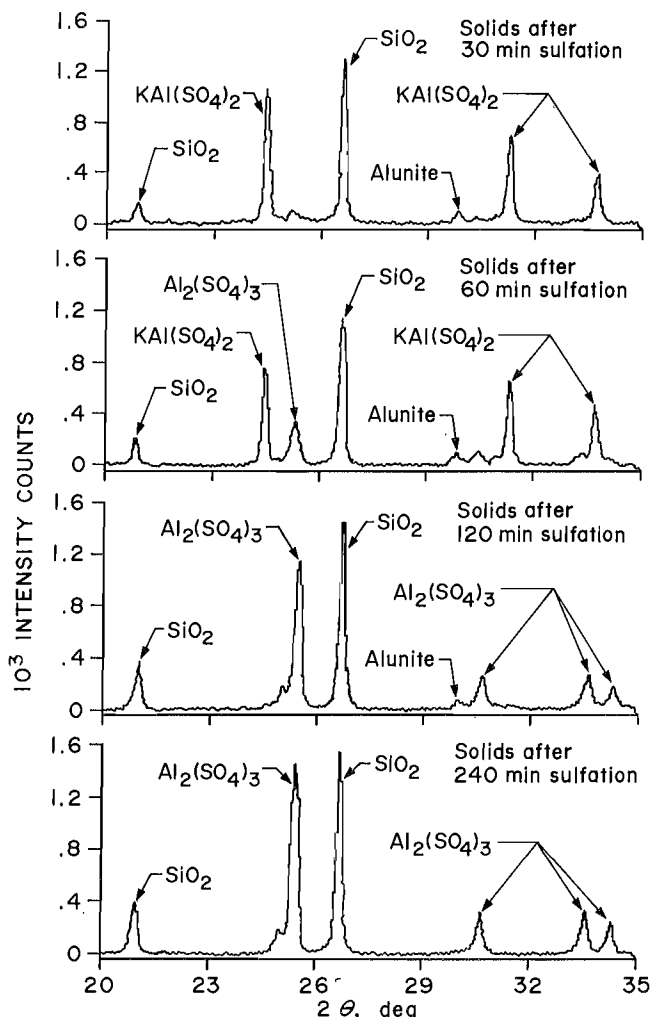
Figure 10.—X-ray diffraction patterns of sulfated solids showing delayed conversion of $KAl(SO_4)_2$ to $Al_2(SO_4)_3$.

88-wt-pct acid and 245° C, reaction C is delayed, as seen in figure 6.

When reactions D and C occur together, the extraction is not affected by changes in acid concentration and temperature, but the overall reaction rate increases significantly with increases in the level of these combined variables, as seen in figure 8. Reaction C is again delayed—this time by the increased concentration of potassium in the acid.

Potassium Control

Analytical results indicated that extracted potassium was present in the acid as potassium hydrogen sulfate $(KHSO_4)$. This compound has a listed melting point of 214° C (14), which means that at the normal sulfation temperatures of 260° C or higher, any $KHSO_4$ not dissolved in

the acid will be in the molten state. Attempts to remove $KHSO_4$ by cooling the acid below 214° C were unsuccessful. Either the $KHSO_4$ remained in solution, or if the $KHSO_4$ concentration was too high, the entire mass solidified.

Two methods showed promise for controlling potassium accumulation in the concentrated acid; either method could be included in a process flowsheet after determination of satisfactory operating conditions. Solubility data for $KHSO_4$ in H_2SO_4 with concentrations above 70 wt pct acid indicate a sharp decrease in $KHSO_4$ solubility with respect to a small decrease in H_2SO_4 concentration (15). Because of this sharp decrease, $KHSO_4$ may be removed from the acid by diluting the bleedstream of the acid from 90 to 80 wt pct and cooling it to ambient temperature. This precipitates accumulated potassium from the bleedstream, leaving a residual concentration of about 20 g/L. The acid may then be reconstituted to sulfation strength by heating to evaporate excess water and recycled to the sulfation system. Precipitated $KHSO_4$ can be converted to K_2SO_4 by calcination. However, this is a two-stage calcination process involving a liquid intermediate product, potassium pyrosulfate ($K_2S_2O_7$) (16), and materials handling could be a problem. K_2SO_4 was produced in this study in small-scale crucible tests.

The other proposed method for potassium control is removal before sulfation. Several processes have been patented for roasting alunite at 600° to 850° C to eliminate chemically combined H_2O and/or SO_2, for leaching the calcined alunite in water or dilute potassium hydroxide (KOH) to remove K_2SO_4, and for recovering Al_2O_3 in a modified Bayer leach (17-23). The presence of sulfate in excess of stoichiometric amounts needed to convert all of the potassium in alunite to K_2SO_4 results in high consumption of caustic reagent in most of these processes. Those processes that eliminate this high reagent consumption do so by calcining $Al_2(SO_4)_3$ to Al_2O_3 in the initial roast, requiring temperatures of at least 800° C.

In dehydration tests conducted as part of the current Bureau study, XRD analyses of alunite calcined at 600° to 650° C showed the presence of major amounts of $KAl(SO_4)_2$. The dehydration can be expressed as follows:

$$KAl_3(SO_4)_2(OH)_6 \rightarrow KAl(SO_4)_2 + Al_2O_3 + 3H_2O. \quad (E)$$
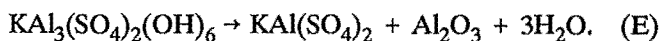
It is presumably sulfate in the $KAl(SO_4)_2$ in excess of that required to form K_2SO_4 that consumed reagent in the dilute caustic leaches performed by previous researchers, according to the following reaction:

$$2KAl(SO_4)_2 + 6KOH \rightarrow 4K_2SO_4 + Al_2O_3 + 3H_2O. \quad (F)$$
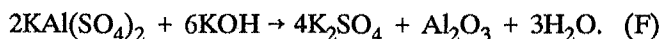
Agitated water-leach tests with the dehydrated alunite ore at atmospheric pressure and temperatures up to 96° C showed very little extraction of aluminum and only 60 to 70 pct extraction of potassium within a pH range of 3 to 6. Above pH 6, potassium extraction was 80 pct or higher, and above pH 10, aluminum extraction increased to near

90 pct. The dilute caustic leaches used by previous researchers are assumed to be in the pH 6 to 10 range, yielding good potassium extraction with no aluminum extraction.

Mixing limestone ($CaCO_3$) with the alunite before dehydration at 600° to 650° C appeared to modify reaction E by forming anhydrite ($CaSO_4$), according to the following proposed reaction:

$$2KAl_3(SO_4)_2(OH)_6 + 3CaCO_3 \rightarrow 3CaSO_4$$

$$+ 3Al_2O_3 + K_2SO_4 + 3CO_2 + 6H_2O. \quad (G)$$
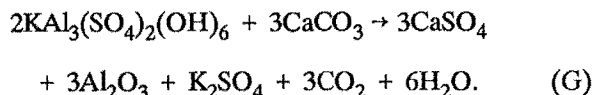
This reaction was verified by roasting alunite with varying amounts of $CaCO_3$ at 650° C for 1 h and analyzing the products by XRD. As $CaCO_3$ additions increased from 0 to 0.3 g/g of alunite, $KAl(SO_4)_2$ patterns in the XRD analyses of the calcine disappeared completely. The XRD analyses showed increasing amounts of $CaSO_4$ up to a $CaCO_3$ addition level of 0.2 g/g of alunite and no increases above that level. Both Al_2O_3 and K_2SO_4 formed in this process were poorly crystallized because neither appeared in the XRD patterns.

Figure 11 shows results of a water-leach test series conducted with alunite ore that had been dehydrated at 650° C for 6 h with added $CaCO_3$. In this series, the addition level of $CaCO_3$ in the dehydration roast and the temperature of the water leach were studied. Leach tests at temperatures up to 96° C were conducted at atmospheric pressure; leach tests at higher temperatures were performed in an autoclave. As shown in figure 11, potassium extraction in the leach solution increased with increasing $CaCO_3$ addition, approaching 90 pct with 0.1 g of $CaCO_3$ per gram of alunite ore. Potassium extraction also

KEY
Leach temperature
● 25° C
▲ 96° C
■ 180° C

Figure 11.—Aqueous extraction of potassium from dehydrated alunite with $CaCO_3$ added during dehydration roasting.

increased with increasing leach temperature, approaching the 90 pct level at 96° C.

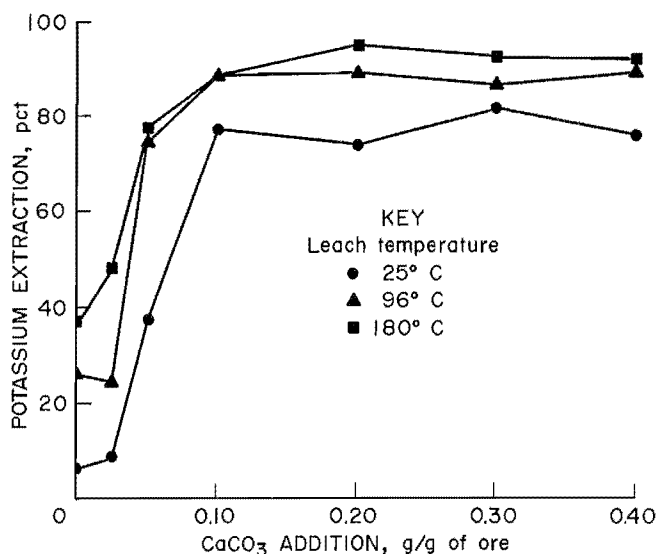Alunite was mixed with 0.2 g of $CaCO_3$ per gram of ore, roasted at 650° C for 6 h, water leached at 96° C with 20-pct solids to remove potassium, and then sulfated in 90-wt-pct H_2SO_4. The roast-leach pretreatment removed 88 pct of the potassium, and the remaining 12 pct reported to the process acid. Aluminum recovery in a water leach of the sulfated material was 98 pct. Potassium concentration in this water leach was less than 0.01 g/L, which is much less than the 0.15 g/L concentration found in sulfation tests without the potassium removal pretreatment.

As stated, this method of potassium control has promise, but it has some perceived disadvantages. Potassium extraction in the water leach following dehydration calcination is sensitive to pulp density in the leach system. Extraction near 95 pct requires pulp densities in the 1- to 5-pct solids range, which is uneconomical, and addition of excess limestone causes high consumption of acid in the sulfation system.

ALUMINUM EXTRACTION

Part of each sulfation test was a water leach of the sulfated alunite to extract the aluminum component as well as other water-soluble components. The standard procedure used in these sulfation tests was a 30-min leach at 95° C with 5 mL of water per gram of sulfated solids. These conditions yielded complete dissolution of all water-soluble components and were a starting point for studying the leaching system.

A three-variable, two-level factorial test was designed to determine the relative effects of leach time, temperature, and pulp density (defined as grams of sulfated alunite slurried in 1 L of leach solution). Alunite was batch sulfated in 91-wt-pct H_2SO_4 at 260° C for 2 h to produce sulfated cake for this factorial test. Potassium extraction into the acid in these sulfation runs was 94 pct, consistently.

Table 2 shows variable levels and aluminum extraction results for the eight runs in this factorial test. Analysis of the data shows that a leach temperature of 95° C resulted in 93- to 94-pct aluminum extraction and completely overshadowed any extraction effects of changes in other variables. This extraction level is identical to the potassium extraction level achieved in the sulfation phase and suggests that extraction of sulfated aluminum was complete. More detailed tests were considered unnecessary because high aluminum extraction could be achieved at relatively high pulp densities within a short period of time.

The leaching reactions are highly exothermic, and a temperature of 50° C was difficult to maintain in these batch tests without an external cooling system. Results from ambient-temperature tests with 400 g of sulfated alunite in 1 L of water solution showed a temperature jump to 92° C within the first 4 min of leaching. Part of this heat comes from the heat of solution of $Al_2(SO_4)_3$, and

TABLE 2. - Variable levels and results in aluminum extraction factorial experiment

Run	Time, min	Pulp density, g[1]	Aluminum extraction, pct
LEACHED AT 50° C			
1	10	400	77.4
2	10	800	68.0
3	60	400	90.4
4	60	800	83.1
LEACHED AT 95° C			
5	10	400	94.0
6	10	800	93.2
7	60	400	93.1
8	60	800	94.0

[1]Grams of sulfated alunite slurried into 1 L of water.

part comes from the heat of dilution of H_2SO_4 entrained in the sulfated alunite. The amount of entrained H_2SO_4 was estimated by assuming that any sulfate in the leach liquor in excess of $Al_2(SO_4)_3$ stoichiometric amounts was present as free H_2SO_4. Assays of typical leach liquor showed about 30 g/L Al and 500 g/L SO_4. The corresponding free H_2SO_4 concentration was 350 g/L H_2SO_4 in the leach solution. These measured values together with the assumption that all of the potassium-containing product of the sulfation was extracted into the process acid yielded a calculated H_2SO_4 entrainment of between 55 and 60 g of H_2SO_4 per 100 g of sulfated solids. This estimated value corresponds very well with the observed weight gains in most sulfation runs.

Carryover of this much H_2SO_4 in sulfated alunite would result in acid buildup in recycled leach solution and could have affected the extraction of aluminum into the water-leach solution. However, results from tests with acid concentration in the leach solution ranging up to 29-wt-pct H_2SO_4 indicated that aluminum extraction was independent of H_2SO_4 concentration over that range. The acid concentration did, however, affect subsequent precipitation of $Al_2(SO_4)_3$ from the leach solution. With increased acid concentration, a greater proportion of the $Al_2(SO_4)_3$ precipitated, but the precipitate also contained more acid.

Overall, results of water-leach experiments show that leaching at 95° C for 10 min or longer with an initial pulp density of up to 800 g of sulfated alunite per liter of solution with initial H_2SO_4 levels in the solution of 29 wt pct or less yields virtually complete extraction of sulfated aluminum.

CONTINUOUS TESTING

Previous batch-type studies on the sulfation and water-leach systems used fresh solutions for each test, and any accumulation of reaction products was approximated by adding reagent-grade chemicals to these fresh solutions. One series of locked-cycle experiments was performed to determine the effects of accumulating actual sulfation and leach reaction products in recycled solutions. These experiments simulated continuous sulfation of alunite, water

leaching of the sulfation residue, and crystallization of $Al_2(SO_4)_3$ from the aqueous leach solution.

Locked-Cycle Sulfation Tests

To determine the accumulation rate of potassium and other elements in the process acid, acid was recycled through 11 successive sulfation tests with fresh alunite. In each of these 11 tests, 500 mL of H_2SO_4 was slurried with 100 g of minus 200-mesh alunite ore and sulfated at temperature for 2 h. The entire sulfated slurry was then filtered hot, and the residue was washed on the filter with 100 mL of fresh acid. The wash was added to the acid filtrate to maintain the acid level near nominal. The acid volume was measured, and the acid was sampled and sent to the next sulfation cycle. Because of the small volumes taken as samples, this removal did not significantly affect the accumulation rate. Solids from the last eight cycles were sent to the locked-cycle water-leach tests.

Assuming complete extraction, potassium concentration in the acid should theoretically increase by about 7 g/L in each sulfation cycle. The first three sulfation cycles were, therefore, conducted at 260° C, corresponding to a nominal acid concentration of 91 wt pct, to take advantage of the rapid potassium extraction at these conditions when the potassium concentration in the acid is 20 g/L or less, as shown in figure 9. Cycles 4 through 11 were conducted at 280° C, corresponding to a nominal acid concentration of 93 wt pct, to assure test result comparability over the bulk of the cycle tests and to take advantage of the better potassium extraction kinetics at these conditions when potassium concentrations in the acid lie between 35 and 75 g/L, also as shown in figure 9. All runs yielded consistent volumes of acid filtrate, ranging from 506 to 515 mL including the wash, and weights of sulfated cake, ranging from 199 to 210 g.

Process acid analyses for the 11 cycles are shown in table 3. Potassium concentration in the acid increased between 4 and 7 g/L per cycle for the first 10 cycles, reaching 61 g/L. During the 11th cycle, however, the potassium concentration increased only 2 g/L, indicating that the potassium was remaining in the solid material as acid-insoluble $KAl(SO_4)_2$. There was also a slow buildup of barium and phosphorus in the recycled acid; however, the saturation level of these elements was not reached in this test series. A small bleedstream could be treated for removal of these elements. The calcium concentration built up to about 9 g/L and then remained fairly constant, indicating that the acid had become saturated. Elements such as aluminum, iron, magnesium, and titanium did not accumulate in the acid.

Based on ore and water-leach residue analyses, total potassium extraction from the alunite was 93 pct or higher throughout all 11 cycles, which is not significantly different from batch-test extractions. Potassium extraction into the acid was 94 pct in each of the first four cycles, decreased gradually to 90 pct in cycle 9, and dropped to 87 pct in cycles 10 and 11. This gradual decrease in extraction into

TABLE 3. - Chemical analyses of sulfation acid in locked-cycle test series, grams per liter

Cycle	Al	Ba	Ca	Fe	K	Mg	P	Ti
SULFATED AT 260° C IN 90-wt-pct H_2SO_4								
1	0.21	NA	1.5	0.06	6.9	NA	NA	0.15
2	.33	NA	3.2	.05	13.5	NA	NA	.05
3	.15	0.29	4.5	.04	20.4	0.01	0.34	.03
SULFATED AT 280° C IN 93-wt-pct H_2SO_4								
4	0.17	0.33	6.0	0.02	27.3	0.01	0.39	0.04
5	.14	.31	6.9	.03	31.9	.01	.46	.03
6	.17	.30	8.0	.03	37.3	.01	.50	.03
7	.18	.47	8.7	.03	42.5	.01	.53	.03
8	.24	.60	9.6	.02	49.0	.01	.60	.03
9	.20	.63	9.4	.02	54.0	.01	.63	.03
10	.23	.64	10.2	.02	61.0	.01	.69	.03
11	.25	.77	9.2	.02	63.0	.01	.71	.03

NA Not analyzed.

the acid indicates that 2 h was not sufficient to complete the sulfation reaction sequence. Previous batch tests with fresh acid loaded with potassium at levels near those attained in these locked-cycle tests had achieved 95-pct extraction of potassium into the acid within 2 h. This suggests that potassium extraction into the acid via reaction C may be dependent on the total dissolved impurity load in the acid and not on potassium loading alone.

Locked-Cycle Water-Leach and Crystallization Tests

Locked-cycle water-leach tests determined the effects of impurity buildup in the leach solution during aluminum extraction and subsequent crystallization of $Al_2(SO_4)_3$. Sulfated alunite from the last eight locked-cycle sulfation runs was leached for 30 min at 100° C in locked-cycle leach tests with an initial slurry mix of 1,000 g of cake per liter of solution. After the insoluble residue was filtered out and washed with fresh water, the leach solution was cooled to ambient temperature to crystallize out $Al_2(SO_4)_3$. After removal of the $Al_2(SO_4)_3$ crystals, sufficient makeup water was added to bring the solution back to volume, and the solution was recycled to the next leach.

Aluminum extraction in this water-leach series was consistently between 92 and 96 pct of the total aluminum in the ore, again indicating that recovery of sulfated aluminum is essentially complete.

Analyses of the leach solutions prior to cooling and crystallization are shown in table 4. Aluminum concentration in these solutions remained fairly constant throughout the cyclical tests, indicating that all of the aluminum leached in each cycle was crystallized out by cooling the solution to ambient temperature. Elements such as iron, magnesium, and titanium increased in concentration to a point and then leveled off, indicating that those elements also began to crystallize with the aluminum and would require removal before an Al_2O_3 product could be obtained. Calcium concentration has an inverse relationship with sulfate concentration, with the increasing sulfate concentration forcing the calcium to precipitate, probably as gypsum.

TABLE 4. - Chemical analyses of loaded water-leach solutions in locked-cycle test series, grams per liter

Cycle[1]	Al	Ca	Fe	K	Mg	SO$_4$	Ti
1	30.6	0.35	3.2	0.11	0.38	520	1.5
2	33.2	.49	4.0	.18	.49	697	1.9
3	34.8	.34	5.1	.38	.64	738	2.6
4	32.2	.50	5.2	.38	.64	747	2.5
5	34.6	.23	5.4	.66	.66	771	2.6
6	35.6	.20	5.7	.68	.70	772	2.8
7	40.4	.24	6.7	1.38	.82	891	3.3
8	36.6	.20	5.7	1.22	.70	801	2.8

[1]Cycle 1 of the water-leach series used sulfated alunite from cycle 4 of the sulfation series.

Potassium and sulfate concentrations increased erratically, with a large increase coming in cycle 7 of the leach tests. Sulfated alunite used in this cycle came from cycle 10 of the sulfation series, and the sharp increase in potassium and sulfate reporting to the water leach corresponds to a decrease in potassium extraction into the acid. As explained before, this distribution shift is due to incomplete reaction of $KAl(SO_4)_2$ with H_2SO_4.

TABLE 5. - Chemical analyses of $Al_2(SO_4)_3$ precipitates recovered during locked-cycle leach tests, weight percent

Cycle	Al	Ca	Fe	K	Mg	SO$_4$	Ti
1	4.6	0.07	0.13	0.004	0.02	41.3	0.05
2	4.2	.10	.19	.007	.02	44.5	.08
3	4.9	.05	.19	.014	.03	46.1	.08
4	4.5	.13	.23	.015	.03	47.8	.10
5	3.9	.04	.25	.031	.03	48.4	.12
6	4.8	.02	.23	.027	.03	50.0	.10
7	4.3	.02	.23	.045	.03	48.4	.10
8	4.9	.01	.20	.041	.03	50.0	.09

Table 5 presents analyses of the $Al_2(SO_4)_3$ crystals recovered during the locked-cycle leach tests. These analyses show that a consistent product was obtained in each cycle. XRD patterns indicate that the raw precipitate was $Al_2(SO_4)_3 \cdot nH_2O$, where n ranges from 16 to 18, and that drying the precipitate for 24 h at 80° C decreased the range of n to between 12 and 14. The precipitate also contained a significant amount of entrained sulfate, caused by the increasing level of acid in the leach solution.

Al_2O_3 PRODUCTION

Al_2O_3 is the much preferred end product of any treatment scheme for processing alunite, but H_2SO_4 processes for producing Al_2O_3 from any source have suffered from severe disadvantages in the past. Two of these disadvantages are (1) very poor filtering characteristics of aqueous $Al_2(SO_4)_3$ solutions, causing huge entrainments of liquor and very slow filtration rates and (2) high energy costs in calcining $Al_2(SO_4)_3$ to Al_2O_3. The current research did not address either of these engineering problems but was intended to examine the chemistry of concentrated H_2SO_4 digestion of alunite. The economic problems involved in producing Al_2O_3 from H_2SO_4 routes remain to be solved.

In the current studies, Al_2O_3 was produced in small-scale quantities to determine the degree of additional purification needed to meet cell-grade specifications. $Al_2(SO_4)_3$ from the locked-cycle tests was dissolved in fresh water and recrystallized to remove entrained H_2SO_4 and other soluble impurities. The recrystallized $Al_2(SO_4)_3$ was ovendried at 100° C for 24 h to remove a portion of the waters of hydration and then calcined at 1,200° C to produce Al_2O_3.

Impurity analyses of the Al_2O_3 product are shown in table 6 together with the corresponding recommended chemical purity specifications for cell-grade Al_2O_3 (2, p. 11). One recrystallization did not purify the $Al_2(SO_4)_3$ sufficiently to meet these specifications. Iron, especially,

is present at levels greatly exceeding the recommended specifications. Iron has been, and continues to be, a very troublesome impurity in all acidic Al_2O_3 processes. Although research in the past has been devoted to iron removal in these processes (24-25), no economical technique has been developed yet. In the absence of a satisfactory iron removal method, Al_2O_3 from the acid sulfation system could be further treated in a modified Bayer-type system to produce cell-grade Al_2O_3.

TABLE 6. - Impurity analyses of product Al_2O_3 compared with cell-grade Al_2O_3 specifications, weight percent

Component	Product Al_2O_3	Cell-grade Al_2O_3[1]
CaO	0.06	0.04
Cr_2O_3	.081	.002
Fe_2O_3	.446	.015
K_2O	.048	.005
MgO	.059	.002
Na_2O	.02	.4
TiO_2	.161	.005
ZnO	.03	.02

[1]Source: McCawley (2, p. 11).

Another possibility is production of an $Al_2(SO_4)_3$ solution for use in the paper industry or in water purification. This application may be more practical than production of Al_2O_3.

CONCLUSIONS

Recovery of Al_2O_3 from alunite could lessen U.S. dependence on foreign sources of bauxite, thus making this country less susceptible to disruptions in the supply of this critical and strategic metal. Acid sulfation of alunite offers a potential technique for accomplishing this recovery. The following conclusions are presented in summary of the current research.

1. Acid sulfation is effective as a first step in treating alunite ore. The reactions as a result of this research are defined, and the products are suitable for further treatment. The economics of well-known $Al_2(SO_4)_3$ processing problems must be considered and resolved before this system can be adopted.

2. A 2-h digestion of minus 200-mesh alunite ore in boiling H_2SO_4 at concentrations of 88-wt-pct acid or higher breaks down the alunite structure and separates potassium and aluminum.

3. Sulfation proceeds in a two-stage reaction: (1) sulfation of alunite to form $KAl(SO_4)_2$, and (2) further sulfation to convert that compound to $Al_2(SO_4)_3$ and $KHSO_4$.

4. Over 90 pct of the potassium was extracted into the process acid using an initial slurry mix of 200 g of alunite in 1 L of acid solution. Potassium accumulates in the recycled acid and must be removed by further treatment. A dilution-precipitation-roasting technique is feasible for recovery of this potassium as K_2SO_4, but the method poses some severe materials-handling problems. Another possibility for potassium control is removal beforehand in a limestone roast and water-leach procedure.

5. Acid-insoluble aluminum compounds were extracted from the sulfated residue in a 10-min, 95° C water leach using 800 g of solids in 1 L of water. Aluminum recovery in this leach procedure was consistently near 95 pct.

6. The acid sulfation and water-leach system was shown to be technically feasible in a continuous system, although more comprehensive continuous testing is highly recommended.

7. $Al_2(SO_4)_3$ can be precipitated from the water-leach solution and calcined to Al_2O_3. Because this Al_2O_3 did not meet cell-grade specifications without further purification, either a purification system must be developed or the Al_2O_3 must be further treated in a Bayer-type system.

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[3]A title enclosed in parentheses is a translation from the language in which the work was published.